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1. Title of the Invention

METHOD FOR MANUFACTURE OF
ULTRATHIN COPPER FOIL

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Specification

1. Title of the Invention

METHOD FOR MANUFACTURE OF ULTRATHIN COPPER FOIL

2. Patent Claims

A method for the manufacture of an ultrathin copper foil by conducting zinc substitution plating on the edge portion of one surface of an aluminum foil or aluminum alloy foil, then conducting copper plating to a thickness of 0.5-12 µm in a copper pyrophosphate plating bath on

the entire surface of said surface, and then conducting copper plating to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

3. Detailed Description of the Invention

The present invention relates to a method for the manufacture of an ultrathin copper foil for high-density printed circuit boards in which a wiring width and wire spacing are greatly decreased.

In recent years, significant progress in electronics technology created a demand for highly reliable high-density printed circuit boards. In particular, in the copper-clad laminates for printed circuits of computers, it became necessary to form ultrafine circuits with a wiring width and wiring spacing of no more than 0.2 mm. However, the thickness of the conventionally used copper foils was as large as about 85 μm . Therefore, in the etching technology at the time, when circuits were formed from such copper foil-clad laminates, there was a danger that the copper foils would be undercut by side etching (a lower side portion of a groove is etched on the periphery thereof and a recess-like portion is obtained), causing a short circuit. For this reason, circuits with high-density wiring widths and wiring spacing could not be obtained. Therefore, it was impossible to obtain highly reliable printed circuits with a high density.

Accordingly, thin copper foils with a thickness of 18-25 μm were used to attain this object. However, since they were manufactured by electrolytic methods similar to those for the manufacture of the above-mentioned thick copper foils, pinholes easily occurred. Moreover, because the foils were so thin, "wrinkles" and "scratches" could easily occur when the foils were handled. A low production yield and a high cost were other drawbacks associated with such ultrathin foils. Furthermore, when such copper foils were employed for forming high-density circuits by a photoresist method, the lower limit for the wiring width and wiring spacing was 0.2 mm, and high-density circuits with an ultrafine pattern having wiring widths and spacing less than this limit were difficult to produce.

An improved method was suggested, this method using an ultrathin copper foil formed by employing an aluminum foil, etc. as a pseudo-substrate and electroplating a copper layer with a thickness of no more than 18 μm thereupon. A glass-epoxy base material was laminated on the copper foil surface, the aluminum foil serving as a pseudo-substrate was removed by chemical or mechanical peeling method, and the resulting copper foil laminated sheet was used to form a high-density circuit by the aforesaid photoresist process. Such a method is disclosed, for example, in Japanese Patent Application Laid-open 48-85857.

However, with such a method, it is necessary to conduct zinc substitution plating on the electrocoating surface of the aluminum foil in advance in order to provide for good bonding strength of the ultrathin copper layer formed by electroplating with the aluminum foil serving as a pseudo-substrate and it was also necessary to dissolve and remove the aluminum and zinc chemically in order to obtain a copper clad laminate after lamination of the glass-epoxy base material. Therefore, in addition to those two types being complicated and wastewater treatment being difficult, there are disadvantages in that the copper layer is partially dissolved when the zinc is removed, and circuit shorts occur easily.

With another suggested method, copper cyanide plating is conducted on one surface of the aluminum foil of the pre-degreased and activated pseudo-substrate. However, in such a case, the copper adhesion strength is insufficient. For this reason, when in subsequent processes a thick copper plating was conducted with an acidic copper plating bath and then treatment was

conducted to increase the adhesive force, the copper layer could be easily peeled off and removed from the surface of aluminum foil. Moreover, when the thickness of the copper plating was less than 12 μm , a large number of fine pinholes were present and the product was not suitable for practical use.

The inventors have conducted an intensive study aimed at the resolution of the above-described problems. Based on the results obtained, a method was developed for the manufacture of an ultrathin copper foil designed for the formation of highly reliable printed circuits with a high density. Thus, with the method in accordance with the present invention zinc substitution plating is conducted on the edge portion on one surface of an aluminum or aluminum alloy foil (referred to simply as aluminum foil hereinbelow), then copper plating is conducted to a thickness of 0.5-12 μm in a copper pyrophosphate plating bath on the entirety of that one surface, and then copper plating is conducted to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

The method in accordance with the present invention will be described hereinbelow in greater detail.

At least one surface of an aluminum foil with a thickness of 30-70 μm (a long foil with a width of 300-1300 mm) is degreased with an alkaline cleaner and washed with water according to the usual procedure. If necessary, washing with water is conducted after pickling with 50% HNO_3 or activation.

Then an edge portion on one surface of the foil is immersed for 2-120 sec in the so-called zincate bath and zinc substitution plating is conducted. In this case, the edge portion as referred to hereinabove is a frame-like portion located on the periphery of the aluminum foil; it has a width of 2-100 mm, preferably, 10-50 mm. This width is referred to as an edge width.

The zinc substitution plating is conducted to improve adhesion of copper layer to the aluminum foil in the portions that are directly subjected to copper plating. Thus, when the end portion of the aluminum foil is not subjected to zinc substitution plating, a copper pyrophosphate plating itself cannot provide for a sufficient bonding strength with the surface of aluminum foil. When, in such a state, water washing and copper sulfate thick plating are performed in the subsequent process, the copper layer can easily peel from the edge portion of the aluminum foil. Moreover, if the coating peels off even slightly, then water or plating solution rapidly penetrates into the interface between the aluminum foil and copper layer, the surface of aluminum foil is corroded mainly by the plating solution, and the peeling is further promoted. Even if the substrates in such a state are finally dried, since the major portion of the copper layer has peeled from the pseudo-substrate, "wrinkles" or a large number of pinholes appear therein, making the foil unsuitable for practical use. However, if zinc substitution plating of the edge portion of aluminum foil is conducted as described above, the bonding strength with respect to the copper pyrophosphate plating bath is also improved and no peeling occurs in subsequent plating in a copper sulfate bath. Moreover, when the copper plating is formed to a thickness of no less than 5 μm , practically no pinholes are formed.

Immediately after completion of the zinc substitution plating, a copper layer with a thickness of 0.5-12 μm is plated by using a copper pyrophosphate plating bath, followed by washing with water. In such a case, no specific limitation is placed on the composition of the copper pyrophosphate plating bath, but it is preferred that the copper concentration be 5-100 g/L, the concentration of potassium pyrophosphate be 100-500 g/L, and the pH be 8-12. As for the plating conditions, the bath temperature is within a range from normal temperature to 70°C, the electric current density is 1-5 A/dm², and the electrolysis time is 5-25 sec.

The copper pyrophosphate plating bath is selected for the purposes of the present invention because the coating obtained with such a bath has better adhesion to aluminum foils than that obtained with other copper plating baths, and, naturally, no peeling occurs in the lamination of laminated base materials for printed circuits. Furthermore, in addition to that fact that stronger adhesion cannot be maintained, it is not necessary to chemically dissolve and remove the aluminum foil pseudo-substrate after lamination of the base material, and peeling can be conducted by a simple mechanical means. As a result, wastewater treatment is made unnecessary, and the aluminum used can be easily recovered in the form of aluminum chips. Furthermore, a copper pyrophosphate plating bath makes it possible to conduct uniform electrocoating, and a coating can be obtained which is smooth and has good gloss. Moreover, a very small number of pinholes appear even when a thin copper foil is obtained. The thickness of the copper pyrophosphate plating is limited to 0.5-1.2 μm for the following reasons. When the thickness is less than 0.5 μm , the number of pinholes in a thin copper foil obtained increases, making it unsuitable for practical use. On the other hand, when the thickness exceeds 12 μm , since the upper limit of thickness of thin copper foils is 15 μm , the copper sulfate plating in the subsequent process cannot be conducted. Moreover, adhesion to plastic laminated base materials is degraded. The thickness of the copper foil layer is preferably 2-7 μm .

Plating copper to a thickness of 8-12 μm in a copper plating bath containing copper sulfate is conducted as a method for roughening of the copper foil layer. Appropriate conditions of such treatment should be selected and no specific limitation is placed thereon. Typically the copper plating bath has a copper concentration of 20-60 g/L and a sulfuric acid concentration of 40-150 g/L. The bath temperature is preferably within a range from normal temperature to 60°C. As for the electric current density and electrolysis time, they are somewhat affected on the liquid flow parameters, stirring state, and plating thickness, but preferably they are usually within the ranges of 5-40 A/dm² and 1-10 min, respectively. The external appearance of the obtained copper plated film must be such that velvety peaks and valleys of red color are formed.

The thickness of the copper plated layer is limited to 8-12 μm for the reasons as follows. The entire thickness of plated copper layer may be 15 μm and the thickness of the plated layer obtained by using a copper sulfate bath may be adjusted by varying the thickness of the plated layer obtained with the above-mentioned copper pyrophosphate plating bath.

The plated layer with the above-mentioned roughening treatment is further laminated with a plurality of layers of a composition prepared by infiltrating an insulating substance such as glass fibers with an epoxy resin, and then the aluminum foil pseudo-substrate is peeled off, thereby obtaining a final product.

In this case, the bonding strength between the plated copper layer subjected to the roughening treatment and said laminated insulating material may be about 1.6-1.8 kg/cm², but if it is less than 1.6 kg/cm², secondary roughening treatment copper plating is conducted on the outer side of the copper plated layer. For this purpose a method can be used in which, for example, cathodization is conducted at a current density of 2-20 A/dm² for 2-120 seconds in an acidic copper electrolytic bath having added therein ions of at least one metal selected from a group including arsenic, antimony, and bismuth.

Embodiments of the present invention will be described hereinbelow

Embodiment 1

A soft pure aluminum foil (99.9%) with a thickness of 70 μm was degreased by immersion for 3 min in a solution of sodium orthosilicate (100 g/L) at a temperature of 70°C, and then pickling and activation treatment was conducted by immersion for 1 min at a temperature of 25°C in an aqueous solution of HNO₃ with a concentration of 350 g/L. Then, an edge portion (edge width 20 mm) on only one side of the aluminum foil was selectively subjected to local zinc substitution plating by immersion for 60 sec in a solution (liquid temperature, room temperature) consisting of ZnO 30 g/L and NaOH 100 g/L. Then, one side of the aluminum foil was plated with copper for 5 min at an electric current density of 2 A/dm² in a plating bath (liquid temperature 50°C) having a Cu concentration of 30 g/L and a potassium pyrophosphate concentration of 150 g/L and a pH of 8.8. Finally, the plated layer was subjected to roughening copper plating for 2 min at a current density of 10 A/dm² in a plating bath (liquid temperature 20°C) containing Cu at 20 g/L and H₂SO₄ at 75 g/L. As a result, an ultrathin copper foil with a copper layer thickness of 6 μm was obtained.

Embodiment 2

A hard aluminum alloy foil (Al 99.7%, Cu 0.05%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 30 sec at a temperature of 50°C in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and nonionic surfactant 0.1 g/L. Then, pickling and activation treatment was conducted by immersion for 30 sec at a temperature of 25°C in a solution consisting of HCl 100 g/L and NaCl 50 g/L. Then, local zinc substitution plating was conducted selectively only on the edge portion (edge thickness 35 mm) on one side of the aluminum alloy foil by immersion for 38 sec in a solution (liquid temperature, room temperature) consisting of ZnO 5.0 g/L, NaOH 200 g/L, and FeCl₃ 5 g/L. One surface of the aluminum foil was then plated with copper for 10 min at a current density of 3 A/dm² in a plating bath (liquid temperature 60°C) consisting of Cu 80 g/L and potassium pyrophosphate 30 g/L, and having a pH of 9.3. Then roughening copper plating of said plating layer was conducted for 60 sec at a current density of 6 A/dm² in a plating bath (liquid temperature 25°C) consisting of Cu at 30 g/L and H₂SO₄ at 100 g/L. Finally, the resulting roughened plated layer was subjected to secondary roughening copper plating for 20 sec at a current density of 6 A/dm² in a solution consisting of Cu (BF₄)₂ 25 g/L, HBF₄ 42 g/L, Na₃AsO₄12H₂O 0.9 g/L (liquid temperature 12°C), and an ultra thin copper foil with a copper layer thickness of 7 μm was obtained.

Embodiment 3

A hard aluminum alloy foil (Al 99.3%, Cu 0.04%, Fe 0.07%, Si 0.15%, Zn 0.05%, Mg 0.10%, Ti 0.05%) with a thickness of 50 μm was subjected to anodic electrolytic degreasing for 30 sec at a current density of 2 A/dm² in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and a nonionic surfactant 0.1 g/L. Then only the edge portion (edge width 15 mm) of the Al alloy foil was selectively subjected to local zinc substitution plating by treating for 20 sec in a solution (liquid temperature 30°C) consisting of ZnO 70 g/L and NaOH 400 g/L. Then, one surface of the aluminum foil was plated with copper for 15 minutes at a current density of 3 A/dm² in a plating bath (liquid temperature 60°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0. Then, the copper plated

layer was subjected to roughening copper plating for 75 sec at a current density of 32 A/dm² in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H₂SO₄ concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm² in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H₂SO₄ at 32 g/L, H₃AsO₄ at 0.4 g/L, and H₂SiO₃ at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 15 μm was obtained.

Comparative Example 1

A hard aluminum alloy foil (Al 99.7%, Cu 0.5%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 3 min in a solution (liquid temperature 70°C) consisting of sodium carbonate 30 g/L and sodium phosphate 50 g/L, and then an edge portion of 15 mm on one surface of the aluminum alloy foil was selectively subjected to zinc substitution plating by immersion for 20 sec in a solution containing ZnO at 70 g/L and NaOH at 400 g/L (liquid temperature 30°C). Then, copper plating was performed on the entirety of one surface of the aluminum alloy foil for 15 minutes at an electric current density of 3 A/dm² in a plating bath (liquid temperature 40°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0, then the copper plated layer was subjected to roughening copper plating for 75 sec at an electric current density of 32 A/dm² in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H₂SO₄ concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm² in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H₂SO₄ at 32 g/L, H₃AsO₄ at 0.4 g/L, and H₂SiO₃ at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of 5 μm was obtained.

Comparative Example 2

An aluminum alloy foil identical to that of Comparative Example 1 was used and degreasing was conducted in the same manner as in Comparative Example 1. Then, copper plating similar to that of Comparative Example 1 was conducted immediately without zinc substitution plating and thereafter roughening copper plating was conducted to obtain an ultrathin copper foil with a copper layer thickness of 5 μm.

The ultrathin copper foils with pseudo-substrates attached thereto, which were obtained in the Embodiments 1-3 and Comparative Examples 1-2 were laminated on base materials infiltrated with glass epoxy and then pressing was conducted for 60 min at a pressure of 25 kg/cm² and a heating temperature of 160°C to obtain a laminated sheet with a thickness of 2 mm. Copper-clad laminated sheets were then obtained by mechanically peeling off the pseudo-substrates of aluminum foils, copper pyrophosphate plating was thereafter conducted to increase the thickness of the copper layer to 15 μm, and the bonding strength and pinholes were measured by the usual method. The results are presented in Table 1.

The bonding strength was measured by applying a peeling force in the direction of 90° to a width of 10 mm. The number of pinholes was counted by illuminating the layer from below a dark room and observing the transmitted light.

Table 1.

	Number of pinholes (holes/m ²)	Bonding strength (kg/cm ²)	External appearance of copper foil
Embodiment 1	2-4	1.6-1.7	Fine velvety peaks and valleys
Embodiment 2	1-2	2.0-2.4	"
Embodiment 3	0	20.-2.4	"
Comparative Example 1	20-100	1.5-1.7	Bulbous peaks and valleys
Comparative Example 2	Very large number	1.4-1.8	"

As follows from the table presented above, the ultrathin copper foils obtained by the method in accordance with the present invention have a number of pinholes substantially less than that in the ultrathin foils obtained by the conventional methods and also have excellent bonding strength.

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5. List of Appended Items

- | | |
|-----------------------------|----------------------|
| (1) Power of attorney | 2 copies |
| (2) Specification | 1 copy |
| (3) Drawings | 1 copy 1 [illegible] |
| (3) (4) Copy of application | 1 copy 3 [illegible] |

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1. 発明の名称

電線接合の製造方法

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明細書

1. 発明の名称

電線接合の製造方法

3. 発明請求の範囲

アルミニウム端子はアルミニウム合金端子の片側面に被覆接着剤を用いて、該側の全周にビロラン接着剤を塗布して0.5～1.2mmの側メッシュを行い、並にその外側に複数個性別メッシュにて8～12mmの側メッシュを行うことを利用とする電線接合の製造方法。

3. 材料の形状を説明

本発明は被覆接着剤に側面を接着して複数化したアルミニウム端子のプリント回路基板接合部の設計方法に関するものである。

近年電子機器の新しい動向に伴い、プリント回路基板においてはあらかじめしてあらわされたもののが要求されており、特に電子計算機のプリント回路基板接合部においては、表面積度に接合部が0.3mm以下の細く細かな断面を形成しなければならない。粗いながらも実用されている

技術は、その厚みが約3.8mmと細く窄いため、現在のエンジニア技術においては、その細幅時と細長さからに起る問題を解決せしめるに、技術者がサイドエンジニアリングよりアンダーコント状(側面の下側部分が用意されたエクステンションされ、くぼみ状で側面がされる状態をいう)となる問題となる。それがあるため、接合部が側面に接する高密度の配線を形成することができず、またシート金属にして且つ細い形状のプリント配線をうるととてもできないものであつた。

従つてこのようを目指して開拓する技術としては、1.8～2.5mm程度の薄肉端子が使用されているが、この場合端部の薄肉端子の柔軟性と引張りの強度とより適応されているため、ピンホールが生成し易く、且つ弯曲のために導線を曲げて、「しづ」「ます」等が表示し易い。又歩留りも高く、コストとなるという欠点があつた。従つてこのような構造をフォトレジスト法により直接露光部を形成せしめる場合の問題點は、露光量は0.3mm以下版といわれ、それ以下の

のパターンを有する高密度樹脂の外皮は表面でかつた。

又この改良方法としてアルミニウム箔等を載せしと、その上に電気ノック等により加熱する以下の時間内にメタセキを形成せしめた各種新規法を用いし、既に落葉木カクスエボウシ高密度アルミニウム箔を用いた時、既存のアルミニウム箔を化学的又は物理的に剥離せしむる時計と、剥離せしとし、これを用いたフォトレジスト膜により高密度樹脂膜を形成せしむる方法が開発されている。

然しながらこの方法は既存メタセキにより剥離せられる高密度樹脂膜のアルミニウム箔とを、よく剥離せしめるためにはアルミニウム箔の剥離剤を塗布せしメタセキしてよく剥離があるとおこなうカクスエボウシ高密度アルミニウム箔を剥離するためには化成的アルミニウムとやかくとて剥離せしむなければならない。且つてその剥離が有効でらう且つ樹脂の剥離が困難であると実用目的を達成する能一體性等とも密接

なる、既存樹脂を生じるい欠点がある。

又他の方法としてすなれば、高分化した酸素アルミニウム箔の片側上にソアン化成タフヤおこなう酸素カルノフヤを行ふこともあるが、この場合の酸素量が十分でないため、その他の工場において、酸性のメタセキにより剥離ノフヤを行い、既に多摩川の向上過程を行つて、剥離層がアルミニウム箔から剥離し、既にしづく且つ剥離ノフヤの大きさが1ミリ以下の大きさでは既存の既存をピンホールが存在し剥離上に現し得るものである。

今既存はかかる欠点を改善するため試験を行つた結果、既存を除して、一、既存のアントラクトを形成するための、既存樹脂の剥離方法を見出したものである。から本剤剤はアルミニウム箔又はアルミニウム板金箔（既下準備アルミニウム箔といふ）の片側表面に既存樹脂メタセキを行つた後、既存樹脂にビロリン酸メタセキにて0.5～1ミリの剥離ノフヤを行い、更にその外側に既存樹脂メタセキ層にて0.5～1ミリ

④剥離ノフヤを行うものである。

本剤剤方針について以下詳細に説明する。

3.0～7.0ミクのアルミニウム箔（既3.0～1.3ミクの長尺用）の少くとも片面を常温のアルカリクリーナー等により脱脂し水洗する。又シビの場合はにより5.0ミクHNO₃等で既洗もしくは過酸化した後水洗する。

次いで剥離の片面の表面を所定レンジケート内中に2～12秒浸漬して、既存樹脂メタセキを施す。またこの場合剥離とはアルミニウム箔の周縁に剥離せしめられ部分をいい、その巾は2～10ミク、壁をしくば10～80ミクである。この巾を最終巾といふ。

而して既存樹脂メタセキを施す理由は既存樹脂メタセキされる部分のアルミニウム箔に対する剥離の容易度を向上せしめるためである。即ちアルミニウム箔の表面に既存樹脂メタセキを施せばい場合にビロリン酸メタセキ自体アルミニウム箔面に対して十分な剥離度を保持し得るためにあり、このような表面において水洗更には要

工場における既存も既存メタセキを下層に、アルミニウム箔の表面から剥離が困難するのみならず且つしても剥離すると既成既存又はノフヤ等がアルミニウム箔と既存との界面に剥離し、既存メタセキにより主としてアルミニウム箔の表面を剥離しつつ剥離層を形成する。このよう既存のものを既存既存に付着するとても既存の大半が既存既存から剥離しているため「しづく」又は既存のピンホールを生じる傾向が見せないものとなる。しかし前記の剥離ノフヤアルミニウム箔の剥離既存既存メタセキを施すことビロリン酸メタセキ層に及ぶる剥離層も既存ノフヤ且つその他の既存既存メタセキ層中にかける剥離もかこらないと既存既存以上の剥離ノフヤを剥離せしめた場合ビンホールは既存など見られないものとなる。

而して剥離既存メタセキを施した剥離層にビロリン酸メタセキ層にヨリ0.5～1ミリの剥離ノフヤを行ひ水洗する。この場合ビロリン酸メタセキ層の既存については特に規定するものではな

Cu 0.0 9 g, Pt 0.0 0 5 g, Bi 0.2 0 g) をオルトケイ酸ナトリウム 1 0 0 g/4, $NaOH$ 3 0 g/4, ノーチン不界面活性剤 0.1 g/4 からなる电解液中に Cu 5 0 °C において 3 0 秒浸漬して脱脂を行い、次いで HCl 1 0 0 g/4, $NaCl$ 8 0 g/4 からなる电解液中に 3 5 °C において 3 0 秒浸漬して脱脂並に活性化処理を行つた後、脱アルミニウム合金箔の片面銀層（銀幅巾 2 5 mm）のみを選択的に Zn 0.5 0 g/4, $NaOH$ 2 0 0 g/4, $PtCl_6$ 5 g/4 からなる电解液（液温、液量）中に 3 0 秒間脱酸せしめ両分层銀電解メッシュを行つた後、次いで脱アルミニウム箔の片面を Cu 8 0 g/4, ピロリン酸カリウム 3 0 g/4, H_3BO_4 1 0 0 g/4 からなるメッシュ浴（液温 6 0 °C）中にかいて 1 0 分間、電流密度 3 A/ dm^2 により脱メッシュを行い、次いで脱アルミニウム浴を Cu 濃度 3 0 g/4, H_2SO_4 1 0 0 g/4 からなるメッシュ浴（液温 2 8 °C）中にかいて 2 0 秒間、電流密度 6 A/ dm^2 により凹凸化鋼メッシュを行つた後、次いで脱アルミニウム箔の片面を Cu 濃度 1 0 0 g/4, ピロリン酸カリウム 2 5 g/4, H_3BO_4 9 0 からなるメッシュ浴（液温 6 0 °C）中にかいて 1 5 分間、電流密度 3 A/ dm^2 にて脱メッシュを行い、次いで脱アルミニウム

を Cu 濃度 5 0 g/4, H_2SO_4 5 0 g/4 からなるメッシュ浴（液温 6 8 °C）中にかいて 7 5 秒間、電流密度 3 2 A/ dm^2 にて凹凸化鋼メッシュを行い、最後に脱凹凸化鋼メッシュの上に Cu 濃度 7 9/g, H_3BO_4 3 2 g/4, H_2AlO_4 0.4 g/4, H_2SiO_3 0.2 g/4 からなる电解液（液温 1 8 °C）中にかいて 3 2 秒間、電流密度 4 A/ dm^2 にて 2 次凹凸化鋼メッシュを行つて电解厚 1 8 μ の电解銀層を得た。

比較例 1

3 0 μ の脱酸アルミニウム合金箔（AL 99.7 %, Cu 0.5 %, Pt 0.0 5 %, Bi 0.2 0 %）を脱ソーダ 3 0 g/4, リン酸ソーダ 5 0 g/4 からなる电解液（液温 2 0 °C）中に 3 分間浸漬して脱脂を行い、次いで脱アルミニウム合金箔の片面銀層 1 5 μ を選択的に Zn 0.7 0 g/4, $NaOH$ 4 0 0 g/4 からなる电解液（液温 3 0 °C）中に 2 0 秒間浸漬して脱酸銀層メッシュを行い、次いで脱アルミニウム合金箔の片面の全面に Cu 濃度 1 0 0 g/4, ピロリン酸カリウム 2 8 0 g/4,

ノーチン不界面活性剤 0.1 g/4 からなる电解液（液温 5 2 °C）中にかいて 2 0 秒間、電流密度 6 A/ dm^2 にて 2 次凹凸化鋼メッシュを行つて电解厚 7 μ の电解銀層を得た。

比較例 2

5 0 μ の脱酸アルミニウム合金箔（AL 99.7 %, Cu 0.0 4 %, Pt 0.0 7 %, Bi 0.1 5 %, Zn 0.0 8 %, Na 0.1 0 %, Tl 0.0 8 %）をオルトケイ酸ナトリウム 1 0 0 g/4, $NaOH$ 3 0 g/4, ノーチン不界面活性剤 0.1 g/4 からなる电解液中にかいて 3 0 秒間脱酸銀層 2 A/ dm^2 により脱酸电解銀層を行い、次いで脱アルミニウム合金箔の全面（銀幅巾 1 5 mm）のみを選択的に Zn 0.7 0 g/4, $NaOH$ 4 0 0 g/4 からなる电解液（液温 3 0 °C）中に 2 0 秒間脱酸せしめて両分层銀電解メッシュを行つた後、次いで脱アルミニウム箔の片面を Cu 濃度 1 0 0 g/4, ピロリン酸カリウム 2 5 0 g/4, H_3BO_4 9 0 からなるメッシュ浴（液温 6 0 °C）中にかいて 1 5 分間、電流密度 3 A/ dm^2 にて脱メッシュを行い、次いで脱酸銀層

を Cu 9.0 からなるメッシュ浴（液温 4 0 °C）中に 1 5 分間、電流密度 3 A/ dm^2 にて脱メッシュを行い、次いで脱メッシュの上に Cu 濃度 5 0 g/4, H_2SO_4 3 2 g/4 からなるメッシュ浴（液温 6 8 °C）中にかいて 7 5 秒間、電流密度 3 2 A/ dm^2 にて凹凸化鋼メッシュを行い、最後に脱凹凸化鋼メッシュの上に Cu 濃度 7 9/g, H_2SO_4 3 2 g/4, H_2AlO_4 0.4 g/4, H_2SiO_3 0.2 g/4 からなる电解液（液温 1 8 °C）中にかいて 3 2 秒間、電流密度 4 A/ dm^2 にて 2 次凹凸化鋼メッシュを行つて电解厚 5 μ の电解銀層を得た。

比較例 3

比較例 1 と同様のアルミニウム合金箔を使用し、比較例 1 と同様に脱脂処理を行つた後脱酸メッシュを行つことなく、直ちに比較例 1 と同様の脱メッシュを行ひ更に脱凹凸化鋼メッシュを行つて电解厚 5 μ の电解銀層を得た。

而して上記実験例 1～3 及び比較例 1～3 により得た脱酸銀付电解銀箔をグラフエダラン电解槽の上に重ね重ね、加熱温度 1 8 0 °C、圧

力 2.5 kN/cm²において 60 分間加圧して、厚さ 2 mm の被覆板とした後、アルミニウム箔の板全体と電極的に引き合して剝離試験とした後、剝離の厚さを 1.5 μm にするため、更にビーリング試験ノックを行い、電圧により剥離力を基にピンホールを測定した。その結果は図 1 図に示す通りである。

まく、剥離力は 1.0 cm 中につき 9.0° 方向の引き裂し力によるものであり、ピンホールは場所にかかって下方から光をみて透過する穴の数をカウントした。

特許番号--16433 図
本発明は従来方法により得た樹脂鋼筋に比して、ピンホールが著しく少く且つ剥離力について優れたものを得る効果を有する。

出願人代筆人 先端士 鮎江武雄

図 1 図

	ピンホール数 (個/cm ²)	剥離力 (kg/cm ²)	鋼筋の外観
実験例 1	2 ~ 4	1.6 ~ 1.7	鏡面ピード状凹凸
2	1 ~ 2	2.0 ~ 2.4	/
3	0	2.0 ~ 2.4	/
比較例 1	20 ~ 200	1.5 ~ 1.7	ラング状凹凸
2	無数	1.4 ~ 1.6	/

上記より甲かの細く平滑な方法により得た結果

5. 添付資料の目録

① 著者証	2通
② 代理人書	1通
③ 代理権限書	2通
④ その他資料	1通

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